ISSN 1070-4280, Russian Journal of Organic Chemistry, 2018, Vol. 54, No. 3, pp. 490–499. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © Ya.A. Vereshchagina, D.V. Chachkov, R.R. Ismagilova, E.A. Vedeneeva, 2018, published in Zhurnal Organicheskoi Khimii, 2018, Vol. 54, No. 3, pp. 482–492.

Dedicated to Full Member of the Russian Academy of Sciences I.P. Beletskaya on her jubilee

Mechanism of Hydrolysis of 2,2-Disubstituted Silocanes and Germocanes and 1-Substituted Silatranes and Germatranes

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Received August 9, 2017

Abstract—According to DFT quantum chemical calculations, hydrolysis of 2,2-disubstituted silocanes and germocanes is characterized by lower energies of activation and slightly lower positive Gibbs energies than the hydrolysis of the corresponding silatranes and germatranes. The annular configuration of the hydrolysis products is stabilized by the transannular interaction N→X (X = Si, Ge) and intramolecular hydrogen bonding.

DOI: 10.1134/S1070428018030181

Over the past decades, metallatranes and their bicyclic analogs, ocanes, have attracted researchers' attention as a new generation of biologically active compounds. The problems, achievements, and prospects of using atranes have been considered in [1]. Theoretical studies of the structure of and hypervalent intramolecular coordination N→X (X = C, Si, Ge, B, P) in some atrane systems have been reported in [2–7], and data on the structure of some ocane systems are given in [7–12].

There are a few publications concerned with mechanisms of reactions of metallatranes and their bicyclic analogs such as silocanes and germocanes with nucleophiles. The mechanism of hydrolysis of silatranol and germatranol was studied in [3] at the Hartree–Fock level of theory. DFT studies of the hydrolysis of 1-hydroxysilatrane, 1-hydroxygermatrane, 2,2-dihydroxysilocane, and 2,2-dihydroxygermocane [13] and of 1-halo(methyl)atranes and ocanes [14] have recently been reported.

Atrane structures are fairly stable to atmospheric moisture in comparison to trialkoxysilanes. Experimental data on the hydrolytic stability of silatranes and germatranes are very limited; a few examples include 1-methyl- and 1-hydroxysilatranes and -germatranes [3]; in addition, the hydrolysis kinetics of 1-substituted silatranes was studied [15, 16]. It was found that stabilization of the *endo* configuration of silatranes and germatranes is largely contributed not only by transannular interaction between the nitrogen and silicon or germanium atoms but also by oxygen and other skeletal atoms, which is reflected in the parameters of molecular orbitals [3]. The authors believe that the hydrolytic stability of silatranes and germatranes is determined mainly by external rather than internal factors: the entropy of the system increases, and the free energy decreases.

In this work we performed theoretical study of the hydrolysis of compounds **1–28** in terms of the density functional theory with B3PW91 hybrid functional and 6-311++ G(*df*,*p*) extended basis set, which showed good results in the simulation of hydrolysis of atrane and ocane derivatives [13, 14]. In all cases, geometric parameters of molecules were fully optimized. The critical points on the potential energy surfaces were identified as energy minima by the absence of imaginary frequencies in the corresponding Hessian matrices and as transitions states by the presence of one imaginary frequency therein. Transition states were assigned to reaction paths by descent toward initial molecule and reaction product. Quantum chemical calculations were performed at the Computational Center of the